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Deviation of Polarity from Linearity in Liquid Mixtures Containing an Ionic Liquid

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Physico-chemical properties of liquid mixtures, in general exhibit deviations from linear behaviour with respect to their composition, arising out of different type of cross intermolecular interactions (both specific and non-specific). These specific and non-specific interactions can however be monitored to obtain the linear mixing in liquid mixtures using pseudo-solvent methodology in such a manner that the interactions causing deviations from linearity are cancelled out and mixtures display linear behaviour.

Ionic liquids (ILs) are the potential materials for energy devices,^{1,2} in addition to their diversified applications in chemical synthesis, separation, extraction, biological related phenomena. However their application in various processes is limited, due to their hygroscopic nature and very high viscosities.³ In order to overcome these limitations, addition of cosolvents to these Coulomb materials has been addressed.^{4,5} Addition of cosolvents to the ionic liquids or mixing of two ionic liquids generally causes non-linear behaviour, which arises due to the partitioning of specific and non-specific intermolecular interactions in the pure systems (A-A and B-B interactions) and new class of cross interactions (A-B interactions).⁶ The linear behaviour of a physical parameter for a given liquid mixture can be defined as the summation of the values of parameter in the pure states of liquids multiplied by their mole fraction in the mixture, while non-linear behaviour of a property is the difference of the measured property and the one calculated from linear mixing. These interactions have strong influence on many of the physical parameters of liquids and have been centre point of research in physical chemistry. Divergent approaches i.e., experimental, theoretical and computational, have been adopted in

the literature to investigate the solute-solvent interactions.⁷⁻¹⁶ Solute-solvent interactions in general are expressed in the terms of solvatochromic parameters, such as solvent polarity (the E_T^N parameter), hydrogen bond donor acidity (α parameter), hydrogen bond acceptor basicity (β parameter) and dipolarity/polarizability (π^* parameter).^{7,8,17} The most commonly used solvatochromic parameter used to understand the solute-solvent interactions in liquids is the E_T^N parameter, which is a normalized form of $E_T(30)$ parameter and can be obtained with the help of UV-visible spectroscopy using Reichardt's dye no. 30 as a solvatochromic probe molecule (For further details, refer to SI-5).^{8,17} In view the diversified application of E_T^N parameter to understand the solvent properties, we have chosen it as a physical parameter to study the non-linear behaviour of liquid mixtures, as polarity of solvents is of extreme use in optimizing chemical process, besides understanding its fundamental aspects.^{7,8,17}

A number of reports are available in the literature describing the polarities (E_T^N parameter) of pure ionic liquids as well as of their binary mixtures with molecular solvents.¹⁷⁻²⁹ Polarities of ionic liquids in general are higher than those of organic polar solvents such as dimethylsulphoxide (DMSO), acetone etc. and are lower compared to water and alcohols such as methanol, ethanol etc.^{17-19,25} E_T^N values for most of the binary mixtures of ionic liquid with organic solvents display large positive deviations from the linear behaviour.²¹⁻²⁷ On the contrary, aqueous mixtures of ionic liquids express large negative deviations from linear behaviour.²⁴⁻²⁹ To understand and to quantify the non-linearity arising out of mixing two liquids has been one of the major challenges in physical chemistry of solutions. The non-linear behaviour of liquid mixtures has central role in understanding the colligative properties, equilibrium thermodynamic properties, protein folding, protein denaturation and nucleic acid chemistry etc.³⁰

In general, a given physical property of a mixture ($P_{mix,id}$) composed of n components, predicted as a result of linear mixing, can be expressed as equation (1).

$$P_{mix,id} = \sum_{i=0}^n P_i^0 x_i \quad (1)$$

where, P_i^0 indicates the value of property (P) of component i in its pure state and x_i denotes its mole fraction in the mixture. The

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deviations from linear mixing (ΔE_T^N) were obtained using the equation (2).

$$\Delta E_T^N = E_T^N_{\text{exp.}} - E_T^N_{\text{lin.mix.}} \quad (2)$$

where, $E_T^N_{\text{exp.}}$ and $E_T^N_{\text{lin.mix.}}$ denote the values of E_T^N parameter for a binary mixture obtained experimentally and those from the use of equation (1), respectively.

In this study, we address an important issue dealing with the neutralization of interactions responsible to offer the deviation in polarity of mixture when compared to the sum of products of polarity of pure liquids and their mole fractions in mixture. To answer this, we present a simplified yet highly effective basic experimental methodology.

The molecular interactions causing the contradictory behaviour of E_T^N values in different binary mixtures have been quantified in the literature.^{21,24,25} It has been observed, in general, that the binary liquid mixtures composed of water show large negative deviations, originating from the presence of the solvent specific interactions and hydrophobic nature of Reichardt's dye.^{9,22,28,29,31-37} In contrast to this, the binary mixtures composed of methanol as one of its component, generally exhibit positive deviations.^{22-24,26,37} It can be understood from the contrasting results obtained in methanol and water mixtures that these two solvents possess the interactions which are responsible for opposite behaviours of E_T^N parameter. It thus, can be assumed that the use of water and methanol will offer the opposing interactions in liquid mixtures and the interactions responsible for positive and negative deviations may be cancelled, giving rise to the possibility of linear mixing at certain specific composition. In view of this, binary mixtures with different compositions of methanol and water have been prepared for their use to obtain linear mixing. These mixtures have been termed as "pseudo-solvents". The "pseudo-solvents" thus prepared are considered to be the new type of pure solvents and not the mixtures of two solvents, possessing hybrid interactions.

In order to carry out the experimental analysis in both associative and non-associative types of solvents we have selected four reference solvents DMSO (non-associative nature), formamide, 1-butyl-3-methylimidazolium tetrafluoroborate ($[\text{C}_4\text{C}_1\text{im}][\text{BF}_4]$) and 1-butyl-3-methylimidazolium dicyanamide ($[\text{C}_4\text{C}_1\text{im}][\text{N}(\text{CN})_2]$) (all three having associative nature). Reference solvent is the solvent in which the possibility of linear mixing has been studied by us. Selection of the reference solvents is based on some of the fundamental requirements of the study i.e., complete miscibility into water and methanol for entire composition range, consistent positive and negative deviations from linear behaviour with methanol and water, respectively and their general importance.

Investigation of the linear mixing in DMSO and formamide as reference solvents:

To determine the solute-solvent interactions in liquid mixtures and to find out the possibility of linear mixing, first all the four solvatochromic parameters (E_T^N , α , β and π^*) have been measured, **Table 1**, for pure solvents with the help of UV-visible spectroscopy (For detailed description, refer to SI-5). Thereafter, the E_T^N values for binary mixtures of DMSO as well as of formamide with methanol

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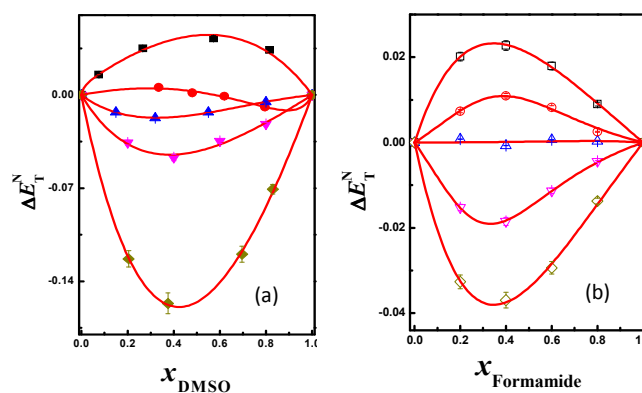


Figure 1: The plots of ΔE_T^N values as a function of (a) x_{DMSO} for binary mixtures of DMSO and pseudo-solvents with methanol: water molar ratios (■) 1:0, (●) 9:1, (▲) 4:1, (▼) 7:3, and (◆) 0:1 and (b) $x_{\text{Formamide}}$ for binary mixtures of formamide and pseudo-solvents with methanol: water molar ratios (□) 1:0, (○) 9:1, (△) 4:1, (▽) 7:3, and (◇) 0:1. Maximum % error: $< \pm 5\%$.

Table 1: Solvent properties of the solvents used in the study

Solvent	E_T^N	α	β	Associative nature
DMSO	0.47 ± 0.01	0.00 ± 0.00	0.70 ± 0.01	Non-associative
Formamide	0.84 ± 0.01	0.71 ± 0.01	0.48 ± 0.01	Associative
$[\text{C}_4\text{C}_1\text{im}][\text{BF}_4]$	0.69 ± 0.02	0.64 ± 0.03	0.64 ± 0.02	Associative
$[\text{C}_4\text{C}_1\text{im}][\text{N}(\text{CN})_2]$	0.63 ± 0.02	0.56 ± 0.02	0.74 ± 0.02	Associative
Methanol	0.76 ± 0.01	1.05 ± 0.02	0.62 ± 0.01	Associative
Water	1.00 ± 0.00	1.10 ± 0.01	0.14 ± 0.01	Associative

and water have been determined and the deviations from linear behaviour were obtained, **Figure 1**, using equation (2). DMSO-methanol mixtures exhibit small positive deviations from the linear behaviour (ranging up to $\Delta E_T^N \sim 0.042$). Since the deviations of E_T^N values from the linear mixing had been assigned to the relative difference of E_T^N values and hydrogen bonding parameters (α and β parameters) of both the solvents in the literature,^{8,17,27} the small positive deviations observed in DMSO-methanol mixtures can be ascribed to be the result of high E_T^N and α values of methanol in comparison to DMSO, **Table 1**. Water-DMSO mixtures on the other hand display large negative deviations, ΔE_T^N values ranging up to -0.157. This differential sort of behaviour observed in DMSO-water mixtures can be credited to very small value of β parameter for water ($\beta = 0.14$) than that of DMSO ($\beta = 0.70$), suggesting the preferential solvation of Reichardt's dye through more basic DMSO. It can be however seen from Table 1 that very high E_T^N and α values of water (1.00) do not have significant role in determining the preferential solvation sphere of dye molecules for DMSO-water mixtures. The binary mixtures comprised of formamide display very small deviations in comparison to DMSO mixtures.

A very important terminology associated with the solute-solvent interactions of liquid mixtures is the associative nature of solvents. The associative nature of the solvents is dependent on the presence

of acidic hydrogens in the solvent molecules i.e., acidic nature of solvents (the α parameter). It can be inferred from the values of α parameter of solvents (Table 1) that formamide, methanol and water are associative solvents whereas DMSO is a non-associative solvent. In spite of having the associative nature, both the methanol and water display contrasting results for the E_T^N values, while mixed with DMSO and formamide. We now point out the significance of β parameter of solvents. The β values of both the DMSO and methanol are comparable and hence the composition of preferential solvation sphere of dye molecules in DMSO-methanol mixtures is determined through high E_T^N and α values of methanol. On the contrary, β value of water is very small in comparison to DMSO, giving rise to a huge preferential solvation interaction in the terms of β value. The negative deviations observed in the DMSO-water mixtures indicate the dominance of β parameter over the E_T^N and α parameters of solvents in determining the preferential solvation composition of dye molecules. Another factor attributed to the negative deviations in water mixtures is the hydrophobic interactions of Reichardt's dye with water,²⁷ which opposes the effects exerted by high E_T^N and α values of water.

Very small amplitude of deviations observed in the methanol-DMSO mixtures in comparison to water-DMSO mixtures, suggests the use of methanol rich "pseudo-solvents" to get the linear mixing with DMSO as a reference solvent. In view of this, the ΔE_T^N values of the binary mixtures composed of DMSO and "pseudo-solvents" possessing the higher compositions of methanol (i.e., methanol: water = 9:1, 4:1 and 7:3) were determined, Figure 1a. The ΔE_T^N values for the binary mixtures of DMSO with the "pseudo-solvent" (methanol: water, 9:1), were found to be surprisingly low, displaying the linear behaviour. The linear fitting of experimental E_T^N values resulted in the value of correlation coefficient $r^2 = 0.9977$ (Figure 2a).

The positive and negative deviations in methanol-formamide and water-formamide mixtures, respectively are observed to be very small compared to that of methanol-DMSO and water-DMSO mixtures. The small amplitudes of deviations can be ascribed to the comparable E_T^N value of formamide with that of water and methanol. The small positive deviations (ΔE_T^N values ranging up to ~ 0.023) in methanol-formamide mixtures are the outcome of higher E_T^N value of formamide in comparison to methanol, whereas the small negative deviations (ΔE_T^N values ranging up to ~ -0.036) in water-formamide mixtures arises out of high β value of formamide ($\beta = 0.48$) than that of water ($\beta = 0.141$) similar to that in water-DMSO mixtures as well as because of the hydrophobic interactions of Reichardt's dye with water.²⁷ The E_T^N values has been determined for the binary mixtures of formamide with varying compositions of "pseudo-solvents" (i.e., methanol: water, 3:2, 1:4 and 1:9) and the resultant ΔE_T^N values have been calculated with the help of equation (2), Figure 1b. The ΔE_T^N values were found to be lowest for the "pseudo-solvent" composition 1:4 (methanol: water), with the value of correlation coefficient for linear fitting $r^2 = 0.9985$ (Figure 2a).

The linear behaviour obtained can be considered as the result of mutual cancellation of solute-solvent interactions responsible for opposing behaviours of E_T^N values. The required amount of basicity (comparable to that of DMSO or formamide) to the "pseudo-solvent" is provided by methanol, which is otherwise not available

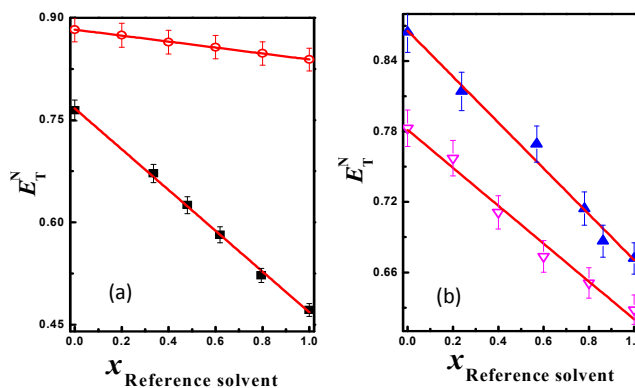


Figure 2: Linear fitting of the E_T^N values obtained as a function of $x_{\text{Reference solvent}}$, (■) for DMSO, (○) for formamide, (▲) for $[\text{C}_4\text{C}_1\text{im}][\text{BF}_4]$ and (▽) $[\text{C}_4\text{C}_1\text{im}][\text{N}(\text{CN})_2]$ at pseudo-solvent compositions 9:1, 1:4, 3:7 and 7:3 (methanol: water molar ratio), respectively. Maximum % error: $< \pm 2\%$.

in water-DMSO or water-formamide mixtures. Simultaneously, the preferential solvation effect caused due to high E_T^N and α values of methanol in methanol-DMSO mixtures and high E_T^N value of formamide in methanol-formamide mixtures gets minimized due to the inclusion of hydrophobic interactions in the mixtures with the introduction of water (as mentioned previously that hydrophobic interactions of water opposes the effect of high E_T^N and α values). Thus, the "pseudo-solvents" with the specific composition provides the interactions similar to DMSO and formamide to the Reichardt's dye molecules, which as a result is expressed in the form of linear mixing.

Investigation of the linear mixing in $[\text{C}_4\text{C}_1\text{im}][\text{BF}_4]$ and $[\text{C}_4\text{C}_1\text{im}][\text{N}(\text{CN})_2]$ as reference solvents:

In order to extend the study to another class of liquids viz., ionic liquids, we have taken $[\text{C}_4\text{C}_1\text{im}][\text{BF}_4]$ and $[\text{C}_4\text{C}_1\text{im}][\text{N}(\text{CN})_2]$ as our reference solvents. The ΔE_T^N values for $[\text{C}_4\text{C}_1\text{im}][\text{BF}_4]$ -methanol, $[\text{C}_4\text{C}_1\text{im}][\text{BF}_4]$ -water, $[\text{C}_4\text{C}_1\text{im}][\text{N}(\text{CN})_2]$ -methanol and $[\text{C}_4\text{C}_1\text{im}][\text{N}(\text{CN})_2]$ -water mixtures were determined, Figure 3. The ΔE_T^N values were found to be exceedingly large (ranging up to 0.076) in $[\text{C}_4\text{C}_1\text{im}][\text{BF}_4]$ -methanol mixtures, exhibiting large positive deviations in comparison to methanol-DMSO mixtures. Since the E_T^N values of both $[\text{C}_4\text{C}_1\text{im}][\text{BF}_4]$ and methanol are comparable, the large positive deviations obtained in these mixtures have been accredited to the formation of special hydrogen bond complex²⁰ and small size and high β value of methanol.²⁷ Special hydrogen bond complex indicates the existence of extended hydrogen bonding interactions between the dye and solvent molecules. This hydrogen bonding complex incorporates the effects of both the hydrogen bonding interaction parameters i.e., α and β and is dominant over both the parameters, it can be assumed that the self associative nature of methanol and ionic liquid is outdone by the effects exerted through the hydrogen bond complex formation. On the other hand, the $[\text{C}_4\text{C}_1\text{im}][\text{N}(\text{CN})_2]$ -methanol mixtures display much smaller positive deviations (ΔE_T^N values ranging up to ~ -0.043). Higher E_T^N value of these mixtures than that of pure solvents

at 0.2 mole fraction of ionic liquid indicate the formation of special hydrogen bond complex and thus giving rise to the small positive deviations in these mixtures.

In contrast to the above mixtures, water-[C₄C₁im][BF₄] and water-[C₄C₁im][N(CN)₂] mixtures show large negative deviations (ΔE_T^N values ranging up to ~ 0.124 and ~ 0.195 , respectively) which again can be considered as the consequence of very low β value of water ($\beta = 0.141$) compared to [C₄C₁im][BF₄] ($\beta = 0.643$)²⁷ and [C₄C₁im][N(CN)₂] ($\beta = 0.74$) as well as of the hydrophobic interactions caused due to water. Though the values of α parameter are much smaller for [C₄C₁im][BF₄] ($\alpha = 0.64$) and [C₄C₁im][N(CN)₂] ($\alpha = 0.56$) than that of water, however the effect exerted through the high β values of ionic liquids is found to be dominant. The E_T^N values of the binary mixtures of both the ionic liquids have been determined with varying compositions of "pseudo-solvents" (i.e., methanol: water, 1:1, 3:7 and 1:9 for [C₄C₁im][BF₄] and methanol: water, 4:1, 7:3 and 2:3 for [C₄C₁im][N(CN)₂]) have been determined and the resultant ΔE_T^N values have been calculated with the help of equation (2), **Figure 3**. The "pseudo-solvents" composed of methanol: water 3:7 and 7:3, were found to be the most suitable candidates for linear mixing in [C₄C₁im][BF₄] ($r^2 = 0.9843$) and [C₄C₁im][N(CN)₂] ($r^2 = 0.9804$), respectively, **Figure 2b**.

The linear behaviour obtained in these mixtures can be attributed to the fact that the effect of low β value of water is compensated by the presence of methanol in the "pseudo-solvent" state. Simultaneously, the interactions responsible for positive deviations in methanol-ionic liquid mixtures i.e., high β value of methanol and hydrogen bond complex are diminished in the presence of water. Because water has very low β value and shows hydrophobic interactions with Reichardt's dye, it does not take part in the formation of hydrogen bond complex formation and thus minimizes the positive deviations.

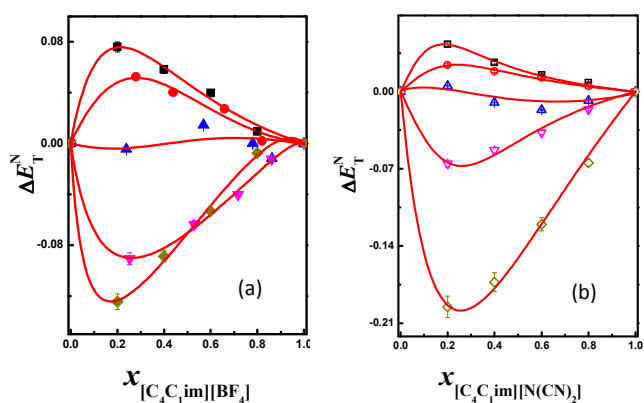


Figure 3: The plots of ΔE_T^N values as a function of (a) $x_{[C_4C_1im][BF_4]}$ for binary mixtures of [C₄C₁im][BF₄] and pseudo-solvents with methanol: water molar ratios (■) 1:0, (●) 1:1, (▲) 3:7, (▼) 1:9, and (◆) 0:1 and (b) $x_{[C_4C_1im][N(CN)_2]}$ for binary mixtures of [C₄C₁im][N(CN)₂] and pseudo-solvents with methanol: water molar ratios (□) 1:0, (○) 4:1, (△) 7:3, (▽) 2:3, and (◇) 0:1. Maximum % error: $\pm 5\%$.

Conclusions

This study deals with the estimation of polarities of liquid mixtures. The differential interactions, which are characteristics of the parent solvents, are diminished and the interactions present in the hybrid "pseudo-solvents" are analogous to the reference solvent i.e., DMSO resulting into linear mixing to offer polarities of liquids. It can therefore, be concluded that a "pseudo-solvent", composed of two or more suitable parent solvents in some specific composition, can serve as the most suitable candidate to replace the reference solvent.

Although the non-ideality in polarity of liquids has been investigated for a variety of physical properties in liquid mixtures, we have, in the above study, explored that the ideal liquid mixtures can be generated using the "pseudo-solvent" methodology, provided the partitioning of the interactions causing the deviations are diminished.

In short, we have proposed a powerful yet simple strategy to convert non-ideality to ideality in liquid mixtures. This is expected to simplify mixing laws in chemistry with far-reaching consequences.

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